This document was prepared in conjunction with work accomplished under Contract No. DE-DE-AC09-76SR00001with the U.S. Department of Energy.

TECHNICAL DIVISION
SAVANNAH RIVER LABORATORY

DPST-78-294
ACC. NO. 109957

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March 30, 1978

M E M O R A N D U M

TO: M. L. HYDER

FROM: E. J. LUKOSIUS EJL

Vitrification of Simulated SRP Sludge by In-Can Melting

INTRODUCTION AND SUMMARY

In-can melting (ICM) is an alternative process to continuous melting for vitrification of SRP high level waste sludge. ICM incorporates calcined sludge into borosilicate glass by using the primary waste canister as the melting crucible. This report describes ICM studies with simulated SRP waste sludge at temperatures ranging from 950-1150°C with no glass pouring and slow cooling rates. Previous vitrification studies with SRP waste have simulated continuous melting by using a melt temperature of 1150° or greater, usually followed by glass pouring and fast cooling rates.[1-4] ICM requires a low glass melting temperature to insure mechanical integrity of the canister.[5]

The laboratory scale studies in this report us l simulated composite[6] oxide sludge (Table 1) and Frits 21 and 21A + $_2CO_3$ (Table 2). Frit 22 (Table 2), a high lithium frit, was also st lied since it forms lower viscosity melts. Temperature and sludge oadings were varied. Microstructural examination and Soxhlet leach[1] tests were conducted on the glasses. These experiments gave the following results:

- o Microstructural examination and leach tests of the glasses indicate that 25 wt % composite oxide sludge (35% washed, dried sludge) can be processed by in-can melting at 1050^0 with Frits 21 or 21A + Na_2CO_3, and at 1000^0 with Frit 22.
- o Frit 22 formed lower viscosity melts than the other frits and allowed more sludge to be incorporated into glass at each temperature.
- o An increase in melt temperature allowed more sludge to be incorporated into glass for each frit.
- o Leach rates increased with increased sludge loadings.
- o At low sludge loadings ($\leq$30%), leach rates decreased with increasing melt temperature.
- o Leach rates of Frit 22 glasses are equal to or lower than corresponding Frit 21 or 21A + Na_2CO_3 glasses.

DISCUSSION

Procedure

Glass melts (50g) were made in small alumina crucibles at 950-1150^{0}C for 3 hours with composite oxide sludge and the three frits at sludge loadings ranging from 25-50%. The melts were slow-cooled to room temperature in the crucibles over ~16 hrs. (The time needed to cool the furnace from 900-500^0 was ~6 hrs at 950^0 melt temperatures and ~8 hrs at 1150^0 melt temperatures.) Each melt was examined for unmelted sludge. Glasses that contained no unmelted sludge were ground to -40 and +60 mesh particles and leached by the Soxhlet[1] method for 24 hrs (Figure 1). Weight losses were recorded and leach solutions were analyzed for sodium content by neutron activation analysis.

Sludge Loadings

The current reference flowsheet for waste vitrification assumes 35 wt % washed, dried sludge will be mixed with 65 wt % frit. This corresponds to 25 wt % composite calcined oxide in the glass.[7] The three frits examined could all incorporate 25 wt % oxide sludge into glass at 950°C (Tables 3-5). However, the porosity of the glasses made with Frit 21 or 21A + Na_2CO_3 begins to increase at temperatures less than 1050° (Figure 2). This suggests that melting rates for these glasses will not meet process needs at temperatures less than 1050°. Porosity increases in similar glasses made with Frit 22 only at temperatures less than 1000°. This is consistent with recent viscosity measurements.[7,8] The viscosity of glasses with 25% composite oxide sludge loadings increases to greater than 200 poise at temperatures less than 1050° for Frit 21 and less than 1000° for frit 22. PNL has indicated that viscosities of <200 poise are necessary for processing commerical waste by in-can melting.[9]

Tables 3-5 show that maximum oxide sludge loadings for each frit increased with an increase in melt temperature.. Frit 22 can incorporate more sludge into glass at a given temperature than either Frit 21 or 21A + Na_2CO_3. In some cases Frit 21 incorporated more sludge than a equivalent amount of Frit 21A + Na_2CO_3. The excess off-gas generated by Frit 21A + Na_2CO_3 melts caused unmelted sludge and high melting alumina to segregate near the top surface. Figure 3 illustrates these differences in glasses that were melted at 1000° with 35% sludge loadings.

Glass Structure

An examination of the microstructure of the glass products showed that devitrification increased slightly with an increase in melt temperature, particularly with Frit 22. Figure 4 shows the microstructures of three Frit 22 glasses under polarized light at 25% sludge loading as a function of melt temperature. An increase in devitrification is apparent. This trend is probably caused by the slower glass cooling rates at higher melt temperatures.

At low sludge loadings (25%), Frit 22 devitrified to a greater extent than the other frits. Figure 5 shows the structures of glasses made with each frit at 1050° and 25% sludge loading. Each is an opaque black or dark brown glass similar to glasses made by other methods.[1-4] However, microstructural examination shows that the Frit 21A glass has some inhomogeneity and devitrification near the top surface. With Frit 22, devitrification is apparent throughout the glass.

At higher sludge loadings, glasses made with both Frits 21 and 21A + Na_2CO_3 showed phase separations near the top surface due to increased viscosity and poor mixing. Frit 22 showed phase separation to a lesser extent and the separations occurred throughout the glass. Figure 6 illustrates these observations with glasses made at 1050^0 and 30% sludge loadings.

In all cases the phase separations consist of an extensively devitrified high alumina phase (nephaline) and a high iron phase that contains spinel crystals (Figure 7).[10]

Leachability

Tables 3-5 show results of 24 hr Soxhlet leach tests on each glass in terms of both percent weight loss and percent sodium lost. The total weight losses of 0.8-4.2% correspond to leach rates of 1.1×10^{-4} - 6.0×10^{-4}g/cm^2-day. The surface area of the glass samples was measured to be 70 cm^2/g by BET surface area analysis. The sodium weight losses vary for 0.7-3.7 wt % (1.0×10^{-4} - 5.3×10^{-4}g/cm^{-2}-day bulk leach rates). In general the sodium leach rates are higher than the corresponding total percent weight loss for a given glass, which indicates sodium is preferentially leached from glass. Despite, large differences in devitrification in glasses as a result of changes in sludge loadings and melt temperatures, the leach-abilitites differ only by a factor of 5 at the maximum. These results are similar to previous leach rate studies with simulated sludge and borosilicate glasses[1] that were made under simulated continuous melting conditions.

Both weight losses and sodium losses show the same trends. With all frits an increase in sludge loading increased the leach rate. At low sludge loadings ($\leq$30%) the glasses generally became more durable as melt temperatures were increased. With Frit 21A + Na_2CO_3 and Frit 22, the leach rate increased at 1150^0, which could reflect the increased devitrification in the glasses.

At higher sludge loadings (>30%), the low viscosity Frit 22 glasses continued to show less leaching at higher melt temperatures. However, with Frit 21 and Frit 21A + Na_2CO_3 the leach rates became more variable at higher sludge loadings. This probably reflects the increased contribution[1-6] of phase separation and devitrification to the leach rate in these high viscosity melts.

Leach rates of the glasses made from the three frits are similar at low sludge loadings ($\leq$35%). However, at higher sludge loadings Frit 22 glasses show better leach rates than either Frit 21 or Frit 21A + Na_2CO_3 glasses.

Program

A similar study to that described in the report is underway for sludges that contain high percentages of iron and aluminum.

A study of the effects of corrosion and air oxidation as a function of melting time and temperature on candidate canister materials with composite sludge and Frit 21 is in progress in conjunction with Nuclear Materials Division. The glass quality from these small canister (1 in. dia.) experiments will be evaluated by microstructural techniques and leach tests.

A scale- up to larger diameter canisters (6 in. dia.) is planned to obtain melting rates with newly developed frit compositions and to obtain samples for mechanical strength tests.

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4. Memorandum: J. R. Wiley to M. L. Hyder. "Leachability of Frit 21 Glass Containing Actual SRP Sludge," DPST-77-541, December 27, 1977.

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6. Memorandum: A. J. Hill, J. R. Wiley and H. D. Harmon to M. L. Hyder. "Description of Aged Savannah River Plant Waste," DPST-77-425, August 23, 1977.

7. Memorandum: M. J. Plodinec to M. L. Hyder. "Long-Term Defense Waste Management Progress Report, Viscosity of Glass Melts, II," DPST-77-455, September 19, 1977.

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9. "Annual Report on Characteristics of High Level Waste Glasses." ERDA Report BNWL-2252. Battelle Northwest Laboratories, Richland, WA (1977).

10. Memorandum: M. J. Plodinec, J. R. Wiley, N. E. Bibler and H. D. Harmon. "Description of SRP High Level Waste Glass," DPST-77-426, September 26, 1977.

EJL:jcn

TABLE 1

COMPOSITION OF SIMULATED "COMPOSITE" OXIDE SLUDGE

Component	wt %
Fe_2O_3	31.6
Al_2O_3	46.4
MnO_2	10.3
U_3O_8	6.1
CaO	3.3
NiO	2.2

TABLE 2

COMPOSITION OF GLASS FRITS

Component	Composition (wt %) Frit 21	Frit 21A	Frit 22
SiO_2	52.5	62.3	52.5
Na_2O	18.5	3.3	15.2
B_2O_3	10.0	11.9	10.0
TiO_2	10.0	11.9	10.0
CaO	5.0	5.9	5.0
Li_2O	4.0	4.7	7.3

TABLE 3

LEACH DATA ON GLASSES CONTAINING COMPOSITE OXIDE SLUDGE AND FRIT 21

% Sludge Loading	Melt Temperature (°C) 950	1000	1050	1100	1150
50	X	X	X	X	2.96 (2.11)
45	X	X	X	2.62 (2.56)	2.99 (2.12)
40	X	X	X	1.42 (1.62)	2.16 (1.92)
35	X	X	1.37 (2.04)	1.11 (1.77)	1.32 (1.59)
30	X	1.15 (1.78)	1.09 (1.84)	0.88 (1.32)	0.90 (0.98)
25	1.28 (2.17)	1.06 (1.57)	0.99 (1.47)	0.90 (1.26)	0.87 (1.03)

__ % Wt Lost

( ) % Sodium Lost

X Unmelted Sludge Present

TABLE 4

LEACH DATA ON GLASSES CONTAINING COMPOSITE OXIDE SLUDGE AND FRIT 21A + Na_2CO_3

% Sludge Loading	Melt Temperature (°C) 950	1000	1050	1100	1150
50	X	X	X	X	4.17 (3.66)
45	X	X	X	X	2.52 (2.23)
40	X	X	X	1.70 (1.93)	1.93 (1.87)
35	X	X	1.39 (1.96)	1.52 (2.06)	1.52 (1.91)
30	X	1.39 (2.12)	1.17 (1.93)	1.02 (1.21)	1.14 (1.77)
25	1.12 (1.79)	1.07 (1.50)	1.10 (1.48)	1.06 (1.11)	1.03 (1.10)

__ % Wt Lost

( ) % Sodium Lost

X Unmelted Sludge Present

TABLE 5

LEACH DATA ON GLASSES CONTAINING COMPOSITE SLUDGE AND FRIT 22

Melt Temperature (^{o}C)

% Sludge Loading	950	1000	1050	1100	1150
50	X	X	X	X	1.44 (1.31)
45	X	X	1.49 (1.58)		
40	X	1.36 (1.41)	1.35 (1.35)	1.00 (1.23)	1.25 (1.40)
35	X	1.42 (1.46)	1.32 (1.28)	0.92 (1.16)	1.26 (1.37)
30	1.38 (1.67)	1.28 (1.40)	1.02 (1.17)	0.86 (0.85)	0.95 (1.10)
25	0.93 (1.20)	1.06 (1.29)	0.95 (1.10)	0.77 (0.71)	0.82 (0.82)

_ % Wt Lost

( ) % Sodium Lost

X Unmelted Sludge Present

Figure 1. Soxhlet Extractor For Leaching Glasses

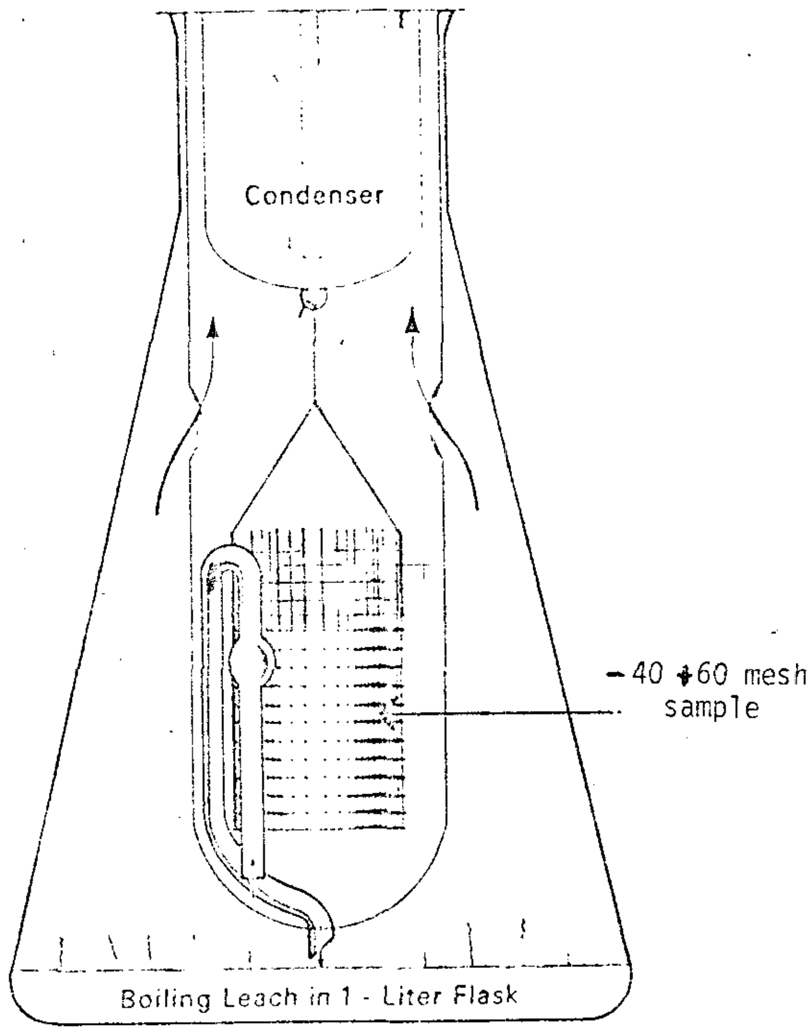
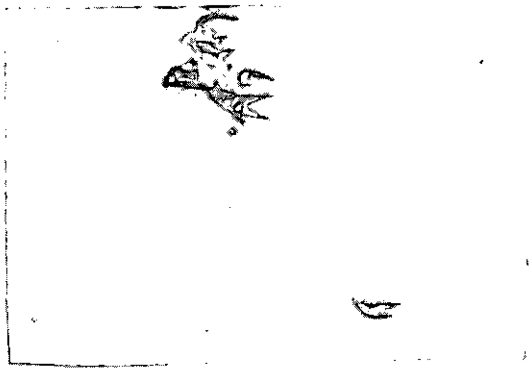


Figure 2.

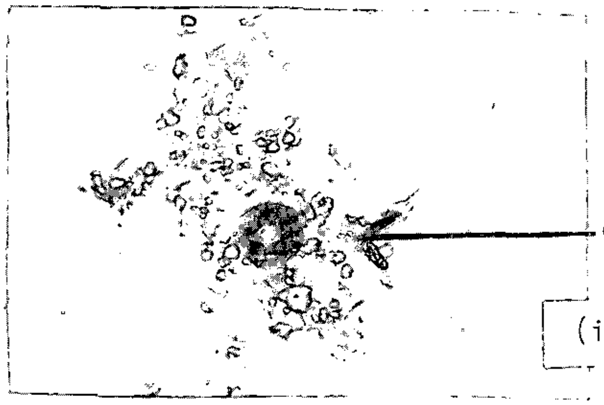
Effect of Temperature on Glass

25% Composite Sludge - Frit 21

225X



1050^{0}



gas bubble

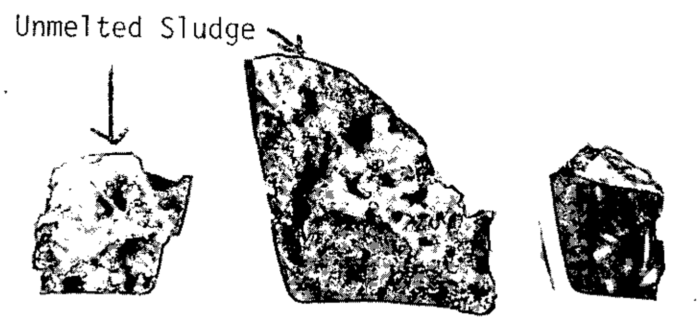
(increased porosity)

1000^{0}

Figure 3. Effect of Frit on Viscosity

35% Composite Sludge

$1000^{\circ}C$



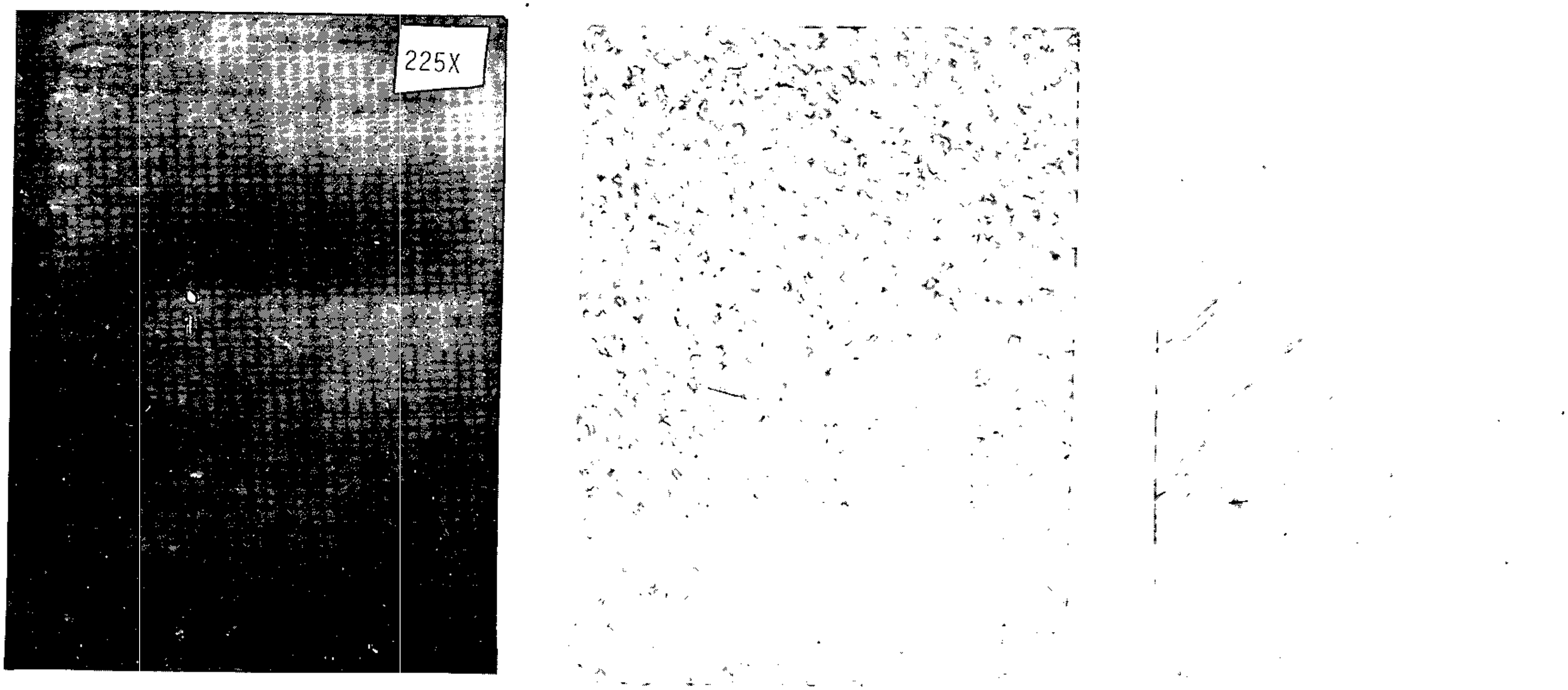
FRIT 21 FRIT 21A + Na_2CO_3 FRIT 22

Figure

Increase in Devitrification with Melt Temperature

25% Composite Sludge - Frit 22

(Polarized Light)



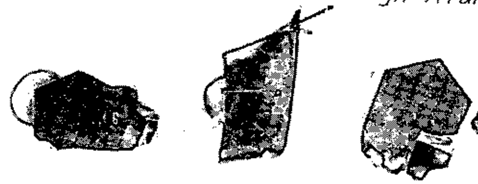
950^0 1050^0 1150^0

Increased Devitrification

Fig. 5.

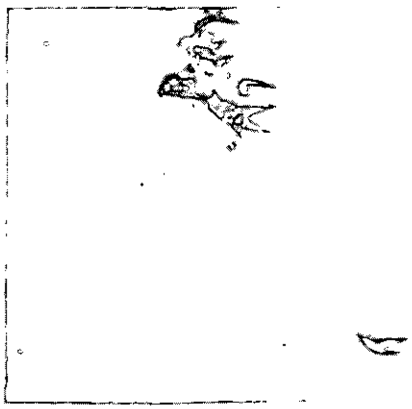
Effect of Frit On Glass Structure

25% Composite Sludge — 1050^{o}

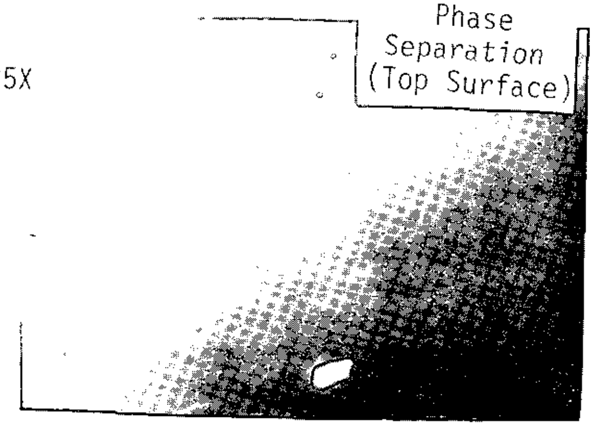


Frit 21 Frit 21A Frit 22

225X

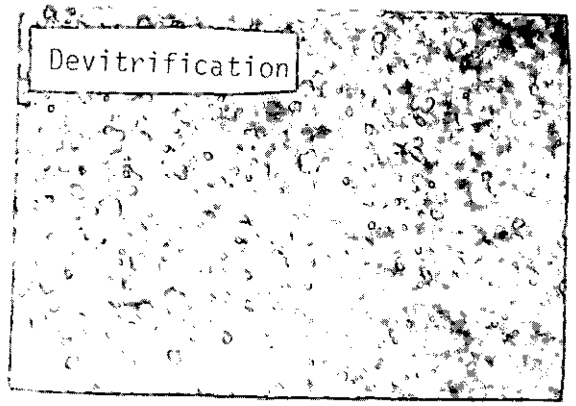


Frit 21



Frit 21A

(polarized light)



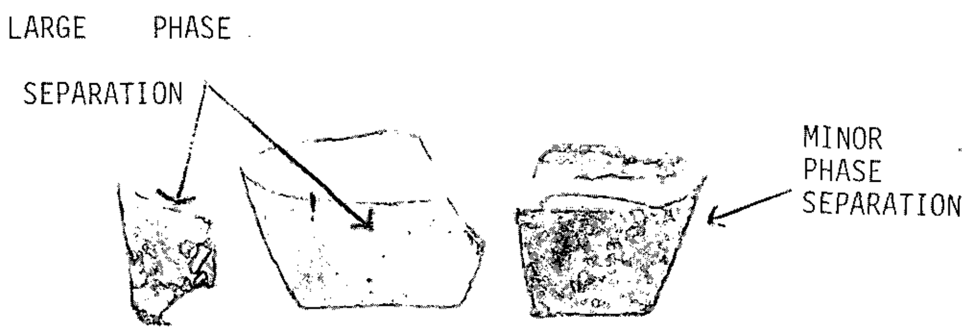
Frit 22

(polarized light)

Figure 6.

Effect of Frit on Glass Structure

30% Composite Sludge — 1050^{0}

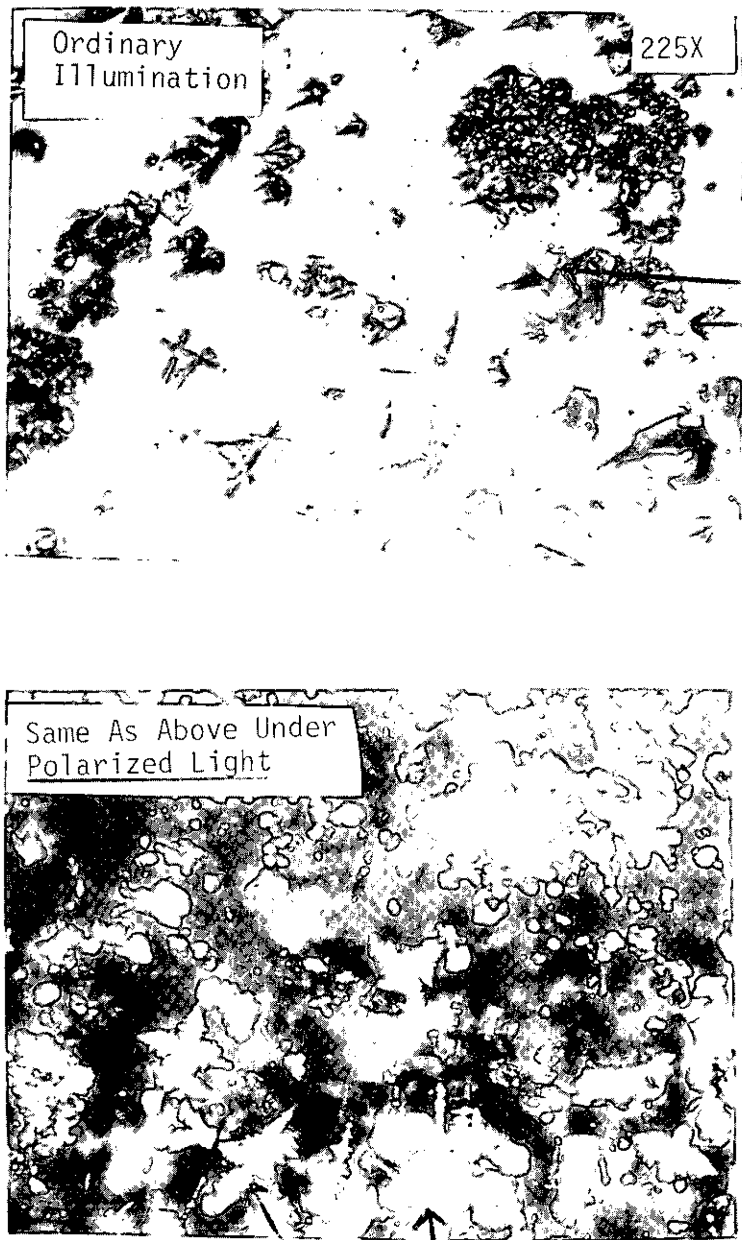


FRIT 21   FRIT 21A + Na_2CO_3 FRIT 22

Figure 7

PHASE SEPARATION IN GLASS

35% Composite Sludge – Frit 21



(High Iron Phase)

Spinels

Nephaline

(High Alumina Phase)